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**A REVIEW OF THE FABRICATION  
AND PROPERTIES OF VAPOR-  
GROWN CARBON  
NANOFIBER/POLYMER  
COMPOSITES (Preprint)**



**Gary G. Tibbetts, Max L. Lake, Karla L. Strong, and Brian P. Rice**

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# **A Review of the Fabrication and Properties of Vapor-Grown Carbon Nanofiber/Polymer Composites**

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## **ABSTRACT**

Several varieties of vapor-grown carbon nanofiber with diameters under 200 nm and conically shaped graphene planes canted with respect to the longitudinal fiber axis are available. Because of the strong inter-fiber bonding, compounding these fibers with polymeric resins demands some care. Therefore, fabrication of nanofiber composites has led to variable and occasionally disappointing electrical conductivity and tensile strength. In the following paper we review the published data for vapor-grown carbon nanofiber (VGCNF) composites and show that the best results, achieved with satisfactory dispersion, are consistent with each other and with calculation. With careful preparation techniques, composite tensile strength and modulus of more than triple that of the neat resin can be achieved with 15 vol% fibers. Electrical conductivity can be achieved with less than ½ volume % fiber loading, while above 15 vol % loading resistivities near 0.1  $\Omega$  cm are possible. Excellent compressive strength and thermal conductivity can also be achieved.

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## **1. Introduction**

### **1.1 The Promise of Carbon Nanofibers**

Vapor-grown carbon nanofibers have occasioned so much interest because they promise to provide solutions to many vexing problems in composite applications. Unlike glass fibers, they are electrically conductive and thus are suitable for applications that require the ability to discharge electrostatic potentials, provide sufficient conductivity for electrostatic painting, or even shield from radio frequency interference or lightning strike. Moreover, their thermal conductivity is excellent.

Because the fibers are discontinuous and not available in aligned form, they presumably will not, in the near term, be oriented in preforms or prepreg tapes to conveniently provide a high level of mechanical strength and stiffness in one or two dimensions, as the randomly oriented clumps of carbon nanofibers currently obtained from manufacturers are not directly suitable for such exacting and expensive fabrication techniques. Nevertheless, efforts currently underway to produce papers fabricated from VGCNF for supercapacitors and fuel cell membrane assemblies may provide a two-dimensionally aligned material applicable to EMI shielding or enhanced planar mechanical properties.

It is much more likely that carbon VGCNF will first be utilized in applications requiring less demanding manufacturing processes. After carbon nanofibers are

compounded with thermoplastics, for example, they may provide a general purpose isotropically reinforced material with properties superior to the neat resin that may be injection molded into improved manufactured articles. Some incomplete alignment can be achieved because of the resin flow during molding, making the composite properties superior to what might be expected with randomly oriented fibers. Furthermore, such articles manufactured from thermoplastics might even be recyclable.

Another class of applications hinges on the small size of nanofibers compared with 7  $\mu\text{m}$  conventionally-sized fibers. For example, the much smaller carbon nanofibers might be inserted between plies of PAN-based or glass fibers to increase the interlaminar shear strength of a composite fabricated from such plies. Moreover, the small fiber will not optically roughen or pebble a composite surface.

Finally, these fibers are being produced in reasonable volumes by several manufacturers and promise to ultimately be less expensive than fibers made of PAN and pitch. Although present prices are several times higher than the US\$ 20/kg level at which the lower grades of PAN are now sold, the low cost of the VGCNF constituents and the inherent simplicity of the fiber growth process give hope that improvements will allow less expensive production.

## **1.2 Development of Carbon Nanofibers**

In the 1970s and 1980s, it was becoming clear that the relatively expensive conventional carbon fibers manufactured from PAN and petroleum pitch could be incorporated in composites to yield excellent properties [1]. Efforts were underway in Japan [2], the Soviet Union [3], the USA [4], and France [5] to efficiently produce “vapor-

grown” carbon fibers from hydrocarbons that would mimic the size and properties of these conventional fibers at more affordable prices. These macroscopic 7- 10  $\mu\text{m}$  vapor-grown carbon fibers, produced from iron catalyst particles in an atmosphere of methane or benzene mixed with hydrogen, were recognized as originating from CVD thickened “filamentous carbon”, and thus could be related to numerous papers dating back to the examination of carbon combustion products in early electron microscopes of the 1950s [6]. Endo reviewed the growth and morphology of these large diameter VGCFs in 1988 [7].

Although difficulties in producing these macroscopic vapor-grown carbon fibers with acceptable efficiencies seemed to be formidable, careful studies indicated that the initial nucleation of the predecessor microscopic carbon filaments was quite efficient. In the reactors producing VGCF, nanometer-sized filaments were made in abundance, but were being submerged and incorporated in the layer of vapor deposited carbon which thickened only a few of the longer filaments to macroscopic [8] dimensions!

An obvious solution was to efficiently and continuously produce the carbon filaments while minimizing the inefficient carbon deposition step. Since the filaments themselves were submicron in diameter, one might envision producing them on a continuous basis and then wafting them out of the reactor with the gaseous production feedstock, thus avoiding the difficult fiber removal step necessary for 7 $\mu\text{m}$  VGCF. Endo et al. [9] reported such a scheme in 1985. A series of papers from General Motors Research Laboratories described development of a process for continuous production of VGCNF utilizing liquid [10] and gaseous [11] catalysts. A helpful review by Lake and

Ting [12] contrasts the properties of the larger diameter VGCF with VGCNF, with particular emphasis on the thermal conductivity of VGCF composites.

### **1.3 Types of carbon nanofibers available**

In the early 1980's, while other groups were still attempting to develop a commercially viable macroscopic VGCF, Hyperion Catalysis ([fibrils.com](http://fibrils.com)) approached the problem of developing carbon nanofibers by first chemically producing dispersed nanometer-sized catalyst particles and then growing “fibrils” from them in reactors using flowing hydrocarbons at high temperatures. These fibrils were relatively long, frequently entangled, and of the coaxial cylinder morphology; they would now be called multi-walled nanotubes. With a very extensive patent policy [13], Hyperion developed commercial allies and a large production capacity, but Hyperion and its users published their results only rarely.

In 1991, Applied Sciences, Inc. ([apsci.com](http://apsci.com)) began marketing a VGCNF developed in collaboration with General Motors Research. These fibers have the stacked-cup morphology, and are manufactured with differing thicknesses of surface vapor-deposited carbon and different surface and debulking treatments at prices in the vicinity of US\$ 200/kg. Partially because these nanofibers have been available in large quantities and at relatively low prices, many groups have experimented with them and published their results.

In Japan, the early work of Endo and collaborators has continued, and more sophisticated understanding of the stacked-cup morphology fiber [14,15] has been developed. Japanese companies such as Sumitomo, Mitsui, Showa Denko, and Nikkiso

have apparently developed sizeable production capacities, and appear to be working on a host of products. However, few composites papers have been published in the open literature, in contrast to a host of papers on the applications of VGCNF to Li-ion batteries [16].

With the discovery of the single-walled carbon nanotubes in (SWNTs) 1991 [17], and its almost instant recognition as a desirable reinforcement material, many organizations sought a practical method of producing carbon nanotubes. Since SWNTs are formed of a single rolled up hexagonal graphene plane, their tightly bonded structure is thought to be advantageous for many mechanical and electrical applications (see the review by Thostenson et al [18]). However, these SWNTs have been available only in gram quantities, and their high cost and poor availability have hampered efforts to exploit the anticipated composite properties. As pioneering work is beginning to be published, it is becoming clear that the Van der Waals interactions between the individual SWNTs, which naturally organize them into ropes of perhaps 100 fibers, are a substantial hindrance to fiber dispersion and hence composite preparation. Nevertheless, expectations are high that the solution of the technical problems of utilizing SWNTs will allow the production of composites with exceptionally useful properties.

A helpful review by Maruyama and Alam [19] describes and contrasts several different types of carbon nanofibers and their applications to composites.

## **2. Production and Preparation of VGCNF**

### **2.1 Growth and morphology**



The Applied Sciences, Inc. process for manufacturing VGCNF is depicted in Figure 1. The primary feedstock is natural gas, while the catalytic iron particles are produced by the decomposition of  $\text{Fe}(\text{CO})_5$ . When the catalyst particles are properly dispersed and activated with sulfur, carbon filaments are abundantly produced in a reactor maintained near 1100 °C.

Figure 2 is a TEM showing the structure of a typical vapor-grown nanofiber. A hollow core is surrounded by a cylindrical fiber grown from a catalyst particle and comprised of graphite basal planes stacked at about 25° from the longitudinal axis of the fiber. Xu et al. [20] have described the lattice continuity conditions which can dictate the formation of nested cone and cone helix morphologies in the core filaments. Figure 3 shows the interior wall of a nanofiber; the nested conical graphene planes are clearly canted with respect to the longitudinal fiber axis. Because the filaments tend to clog the rear of the reactor tube, eventually spending many seconds within the decomposing methane atmosphere, a layer of vapor-deposited carbon both thickens the individual fibers and cements them together in large clumps (Figure 4). The exterior layer of vapor-deposited carbon is not as graphitic as the interior cylinder, and has graphene planes which are primarily longitudinally oriented. By adjusting the feedstock compositions and furnace operating conditions, different thicknesses of vapor deposited carbon can be produced.

## **2.2.Debulking**

In their 1999 study of VGCNF/polymer composites, Tibbetts and McHugh [21] determined that composite voids could be effectively reduced by first ball milling the VGCNF in a Spex shaker mill to decrease the fiber clump diameter to below 0.2 mm. The

authors showed that the clump diameter should be less than the permeation depth of molten polymer through the entangled fibers. Although shaker mill processing is excellent for breaking fiber clumps to uniform size, it is impractical for processing larger fiber volumes on an industrial scale.

Patton et al. [22] compared fibers which had been preprocessed by 15 hours of wet roller milling to unprocessed fibers and determined that the methods of compounding the fibers (section 3 below) were very significant. Using compounding methods designed to preserve fiber length, both epoxy and polyphenylene sulfide composites increased flex modulus with up to 20 vol % VGCNF. Many other experimenters have used single and twin screw extruders with poorer results. Particularly when the fibers are compounded with solid polymer pellets it has been found that fiber breakage diminishes composite quality markedly.

Since debulking without undue fiber shortening is such a difficult problem, it should best be carried out in the fiber manufacturing facility; manufacturers are moving towards solving this problem.

### **2.3 Surface treatments and functionalization**

Making optimal composites of fibers requires adequate fiber-matrix adhesion, which is governed by the chemical and physical interactions occurring at the fiber-matrix interface. If the fiber-matrix adhesion is poor, the composite may fail at the interface, reducing in particular the tensile strength of the composite. While an extensive literature describing the surface treatment of conventional carbon fibers by such methods as oxidation in the gas and liquid phases and anodic etching [23] exists, comparable work is still rudimentary for

carbon nanofibers.

Surface treatments that have proven useful for VGCNF include etching in air near 400 °C, soaking in sulfuric/nitric acid mixtures, or soaking in peracetic acid. These treatments can add enough oxygen so that  $\frac{1}{4}$  of the fiber's surface is comprised of oxygen atoms [24].

P. V. Lakshminarayanan et al. [25] studied VGCNF which had been oxidized with nitric acid. Acid treatment covered the fiber surface with shallow micropores and made the fibers dispersible in water; while XPS measurements showed up to 22% surface oxygen coverage.

In polypropylene composites, it appears that modest surface oxidations, up to 4 % surface oxygen atoms, makes composites with optimum tensile strengths [24]. Further increases in oxygen concentration appear to decrease composite tensile strength. This behavior was attributed to the less polar behavior of the low energy surface of polypropylene, which may have difficulty bonding to a highly oxygenated nanofiber surface.

However, composites made with epoxy give improved tensile properties with the nanofiber surfaces strongly oxidized [26]. Lafdi and Matzuk reported a 35% strength improvement and a 140% modulus improvement with only 4 wt% loading of highly oxidized VGCNF.

Recently, Baek et al. [27] have shown that grafting an aromatic (ether-ketone) to VGCF by polycondensation of the monomer can not only improve compatibility with aliphatic and aromatic matrices, but also aid in dispersing the VGCNF.

Potentially the cheapest and most efficient method of modifying the VGCNF surfaces is to alter the reactant mix within the fiber growth reactor. Glasgow and Lake [28] have patented a scheme utilizing the addition of oxidizing gases, preferably the mild oxidizer  $\text{CO}_2$ , to increase both the surface area and surface energy of VGCNF. More advanced implementations will include flowing the surface modifying gases into specific portions of the growth reactor determined to be most effective, while minimizing deactivation of the vital growth catalysts.

## **2.4 Heat treatments**

Carbon nanofibers having a filamentary core of conically nested graphene planes preferentially recrystallize into discontinuous conical crystallites after a graphitizing heat treatment above 2800 °C (Figure 5). This discontinuous structure improves the crystallinity of the carbon but does not give optimum mechanical or electrical properties to composites in which they are used, or even the lowest resistivity to the fiber itself. This is because the short, nested conical crystallites interface with grain boundaries that lower the fiber's longitudinal mechanical strength, stiffness, and electrical conductivity.

The optimum heat treatment temperature for composite mechanical properties and electrical conductivity [29] lies near 1500 °C, and may vary depending on the specific application. This optimum is achieved when the graphitization of the vapor-deposited carbon exterior layer is maximized in the direction of the fiber's axis (Figure 6). Further heat treatment generally recrystallizes this layer on the conical interior planes, sacrificing its desirable longitudinal properties.

## **3. Composite Preparation**

### 3.1 Dispersion in thermoplastics

Once the VGCNF have been debulked, they must be mixed with polymer and dispersed uniformly, yet high shear mixing which might substantially reduce the length of the fibers must be minimized. For thermoplastics, several dispersion methods have been reported. The simplest was blending in a Minimax injection molder's crucible [21], which uses a rotary cylinder to mix the polymer melt with fibers added by hand. This takes several minutes and has proven to be effective while minimizing fiber breakage, but is limited to small samples.

A hopeful and ambitious study of dispersion in nylon was carried out by van Hattum et al. [30], who used extensive calculations coupled with a "Multi Objective Evolutionary Algorithm" to optimize the performance of a single screw extruder. They achieved optimal composite properties by adjusting the extruder parameters to minimize the weighted average total strain suffered by a fiber during compounding, a clear indication that preserving fiber length was crucial.

Zeng et al. [31] extruded 4 mm in diameter samples from a twin screw extruder and then melt spun 60  $\mu\text{m}$  threads of polymethyl methacrylate reinforced with VGCNF. For both types of material they were able to achieve an 80% improvement in modulus with a 5 wt% loading of VGCNF, although tensile strength did not improve. With a 10 wt% loading of VGCNF the 4 mm samples showed a substantial decrease in modulus, while the 60  $\mu\text{m}$  threads showed only a slight decrease, presumably because the melt spinning step improved dispersion. These indications of dispersion problems underscore the problems of compounding VGCNF with a twin screw extruder.

Since the VGCNF are so small, it is always challenging to measure dispersion of these nanofibers in a medium. Anderson et al. [32] have attacked this problem by combining several light and x-ray techniques to generate a collective scattering curve that yields structural information about the rod-like fibers, inter-fiber spacing, and morphology of the individual fibers.

### **3.2 Dispersion in thermosets**

Patton et al. [22] experimented with two different methods of VGCF/epoxy composite preparation. In the first, they diluted Epon 830 with acetone for lower viscosity fiber infusion, while in the second they used 3000 rpm blending of the fibers with a low viscosity (Clearstream 9000) resin followed by two hours of two-roll roller milling. Both methods were successful, giving up to three and fourfold improvement in flex modulus and more than doubling flex strength.

Because of the high viscosity of thermosets, an approach patented by Wang and Alexander [33], diluting the polymer before fiber dispersion followed by removal of the diluent after dispersion, is particularly useful. This method has been successfully implemented by diluting an epoxy and fiber mix with tetrahydrofuran, agitation, adding the curing agent, removing the solvent, and curing.

Rice et al. [34] utilized high shear mixing of VGCNF into Epon 862 epoxy before wet lay-up and autoclaving with IM7 carbon fiber fabrics. Although this method was only partially successful because the nanofibers could not completely penetrate the fabric, modest improvements in mechanical properties and good improvements in thermal conductivity were obtained.

### **3.3 Orienting Fibers in VGCNF Composites**

It has been shown that the flow field associated with injection molding causes some partial orientation of CNF in the flow direction [35]. Recently, increases in the compressive strength of thermoset composites cured under magnetic fields at the National High Magnet Field Laboratory in Florida have shown some magnetic alignment, presumably due to the anisotropy of the fiber's magnetic susceptibility [36]. Alignment of Showa Denko graphitized VGCNF in a suspension of silicon oil in moderate electrical fields has been optically demonstrated by Takahashi et al. [37]

## **4. Composite Properties**

### **4.1 Electrical**

#### **4.1.1 Intrinsic Fiber Conductivity**

Endo et al. [38] first reported the intrinsic conductivity of large diameter VGCF and the increased conductivity which could be obtained by graphitization at temperatures approaching 3000 °C. Heremans [39] measured resistance of VGCF vs. temperature as a function of heat treatment temperature and related the improvements to increased electron mobility and higher electronic conduction band occupation. The numbers which define the intrinsic limits for composites fabricated from VGCNF are the intrinsic resistivity at room temperature of VGCF grown near 1100 °C,  $2 \times 10^{-3} \Omega \text{ cm}$ , and the room temperature resistivity of graphitized VGCF,  $5 \times 10^{-5} \Omega \text{ cm}$ , which is near the resistivity of graphite. These numbers are consistent with resistivities expected at the observed graphitization indices of the VGCNFs [40].

#### **4.1.2 Conductive thermoplastic composites**

Since virtually all of the electrical conductivity in carbon fiber/polymer composites is through the network of carbon fibers, it is clear that good fiber dispersion, small fiber diameter, and maintenance of fiber length will all aid in achieving high composite conductivity. There are really two goals to be sought in fabricating CNF/polymeric composites. The first is a low percolation threshold; it is achieved when a small volume fraction of fibers first establishes this conducting network. The second goal is achieving sufficient conductivity at high fiber loading to meet more ambitious high conductivity goals, such as radio frequency interference shielding. A further consideration in establishing composite conductivity is that it is a real benefit to maintain any possible fiber clumping interconnects established during the CVD step, as depicted in Figure 4. In contrast to the improvement one receives by breaking these interconnects to obtain adequate dispersion for achieving good mechanical properties, preserving a mesh of interconnected fibers may be may favorable for fabricating composites with good conductivity.

Some fundamentals of the electrical conductivity of VGCNF/poly composites were reported by Goravev et al. [41] in 2000. They found complex time and voltage dependent changes in composite resistivity as the fiber network adjusted to current flow. In a later publication [42] they demonstrated that orienting the VGCNF in a thread of polymer actually reduced the overall conductivity, presumably because of poor transverse coupling between the longitudinally disposed fibers.

In 2001, Finegan and Tibbetts [43] reported extensive conductivity measurements for VGCNF/polypropylene and nylon composites. They found a percolation threshold



around 3 volume % (6 wt %) and were able to reach resistivity values as low as  $0.15 \Omega \text{ cm}$  at about 20 volume % fiber loading. Low temperature (liquid helium) measurements indicated that the resistivity decreased with increasing temperature, consistent with the notion that the resistivity of these composites was limited by a 1 meV “hopping” barrier between the fibers. Cleaner fibers were found to give better conductivity, with graphitized fibers giving the best values of all. Furthermore, although a two minute shaker mill treatment was utilized to make low void composites, longer milling treatments which decreased fiber length were shown to strongly diminish composite conductivity. Later work demonstrated that by processing the fibers more carefully to avoid breakage, the percolation threshold (Figure 7) was lowered to  $\frac{1}{2}$  volume % (1 wt%) of fibers [44].

Xu et al. [45] were able to fabricate conducting VGCNF/vinyl ester composites, investigating a variety of compounding techniques including 3000 rpm mechanical stirring and Braebender mixing with roller blades. Good percolation thresholds of 2-3 wt% were obtained, but resistivities at high weight fraction below about  $10 \Omega \text{ cm}$  were not achieved, probably due to imperfect fiber dispersion. The flex strength of these composites was always less than that of the resin, underscoring the dispersion problem.

Recent work by Zhang et al [46] illustrates the promise of making sensors for organic vapors from VGCNF/polystyrene composites, as the electrical resistivity of such composites rises sharply on exposure to organic vapors. In contrast to structural changes induced in carbon black composites, VGCNF composites cycle reproducibly in vapors such as THF or benzene.

#### **4.13 Electromagnetic shielding**

Conductivity values for VCGNF/resin composites are sufficiently high to offer significant protection from electromagnetic interference. Donohue and Pittman [47] have measured a 45 db shielding effectiveness at 200 MHz for 15 wt% high temperature heat-treated VGCNF in a vinyl ester matrix. The samples were 1.8 mm thick. As one might expect, meaningful differences were found for different composite preparation (fiber dispersion) techniques, indicating that this will be a key issue in fabricating future shielding materials.

## **4.2 Mechanical**

### **4.21 VGCNF mechanical properties**

Unfortunately, direct measurement of the tensile properties of a single VGCNF is a vexing experimental problem and data has not, as yet, been reported. However, direct measurements for the progenitors of VGCNF, the macroscopic vapor-grown carbon fibers have given values of 2.9 GPa for the tensile strength and 240 GPa for the tensile modulus [48], values comparable to a modest grade of PAN carbon fiber. Remember that the morphologies of these fibers are fundamentally different, with the macroscopic VGCF almost totally comprised of nesting coaxial vapor deposited carbon, resembling only the VGCNF's exterior layers, while the interior catalytically formed nesting truncated cones of the VGCNF have more completely graphitized planes, but of off-axis orientation.

To extract intrinsic fiber mechanical properties from composite properties would require that fiber position and orientation within the composite and fiber coupling with the matrix be under good control. As we shall see below, this is somewhat beyond present reach.

#### **4.21 Composite tensile properties**

In 1999, Tibbetts and McHugh [21] published a study of the mechanical properties of VGCNF/polypropylene and nylon composites. The best of these composites, fabricated with a MiniMax hand injection molder, were able to more than double the tensile strength and more than triple the Young's modulus of the neat resin. The most important factor in obtaining these desirable results was breaking up any clumps of fibers to allow infiltration of the molten polymer. A clean fiber surface was also found to be important for achieving the highest values of tensile strength, with modulus being less sensitive to cleanness. A later study was able to demonstrate further improvements in tensile strength for fibers that had undergone more careful surface processing [40]. This work showed that VGCNF/polypropylene composites could be fabricated with more than triple the modulus and tensile strength of the neat resin. Having a more graphitic surface appeared to be a detriment to forming strong polypropylene composites, perhaps because of low surface energies of both the polymer and the fiber. For the very best values, limited oxidation of the fiber's surface was necessary.

In 2000, Kruiger and Alam [49] published a study of VGCNF reinforced polypropylene that demonstrated a tensile strength improvement of a factor of 2.3 at 17 vol% of fibers. Their experimental results showed good agreement with a theory based on x-ray determination of fiber orientation and SEM measurements of average fiber length.

VGCNF can also achieve the same high levels of mechanical properties in thermoset resins. Lafdi and Matzek [26] fabricated Epon 862 epoxy composites from three different types of VGCNF. The best modulus increase, about a factor of 3 higher than the

resin, was obtained from highly surface oxidized oxidized VGCNF, while the largest thermal diffusivity increase was obtained using high temperature graphitized VGCNF. Above 12 wt% of fibers, dispersion became difficult enough so that the mechanical, but not the thermal properties declined.

#### **4.22 Compressive Properties**

Schadler et al. [50] demonstrated that in epoxy/multi-walled nanotube composites, compressive strength increased more than tensile strength, a fact which they attributed to more complete coupling to the interior of the MWNT during compression.

Similar results have been obtained for VGCNF. Kumar et al. [51] spun 55  $\mu\text{m}$  threads of 5 wt% VGCNF in polypropylene which showed encouraging fiber alignment, giving a 16% improvement in tensile strength, a 50% improvement in modulus, and a 100 % improvement in compressive strength over the matrix resin.

A US patent was granted to Ishikawa et al. [52] for using CNF to reinforce resin used between the plies of a composite to increase compressive strength. Their work shows a measurable increase in compressive strength due to 20-35 wt% VGCNF reinforcement, but surprisingly little change in compressive modulus. These high loadings of VGCF were obtained by stirring followed by vacuum deaeration.

#### **4.23 Delamination**

Sadeghian et al. [53] used a 1 wt% mixtures of VGCNF to ameliorate delamination of glass fiber/polyester composites fabricated by vacuum-assisted resin transfer molding. Composites fabricated without VGCNF delaminated at low transverse stress, while composites with reinforcing VGCNF successfully bound adjacent glass tows to diminish

delamination.. Quantitative measurements showed that the VGCNF-reinforced material required a 100% increase in the critical energy release rate at which cracks propagated perpendicular to the applied load to delaminate.

#### **4.24 Damping**

Because nanofibers can reinforce plastics to improve composite modulus and strength without totally sacrificing the high damping loss properties of the neat resin, there is substantial hope that VGCNF can find a role in producing composites helpful for many types of damping applications. Finegan et al. [35] have shown that damping is very dependent on the surface properties of the CNF; nanofibers surface treated to adhere well to polypropylene yielded composites with diminished damping compared to those with poor surface adhesion.

An exploration of the damping behavior of the PMMA/VGCNF composites described above by Zeng et al. [31] similarly showed an increase in dynamic modulus coupled with a decrease in damping losses associated with a 1-5 wt% loading of CNF. However, as the composite began to soften near 100 °C, the damping increased with temperature, which the authors attributed to the enhanced thermal conductivity of the composite.

### **4.3 Thermal**

#### **4.31 Ablation Resistance**

A good example of the multifunctionality of VGCNF is provided by its application in ablation resistant rocket motor insulation, where flame and moisture resistance, decreased composite permeability, and electrical charge dissipation are required in varying

degrees. VGCNFs may make a useful contribution in this field, as they have been able to improve the ablation resistance of both phenolic resins and thermoplastic elastomers [54]. Patton et al [55] have determined that the low erosion and char rates of VGCNF/phenolic resin composites under a plasma torch at 1650°C are very promising for producing solid rocket motor nozzles. Moreover, the VGCNF length can be shortened to produce a lower thermal conductivity than the competing continuous carbon fibers.

#### **4.32 Thermal Conductivity**

In their 1999 paper, Patton et al. [22] measured thermal conductivities of up to 0.8 W/(m K) for 40 vol% VGCNF composites in epoxy. This disappointingly small increase over the neat resin value of 0.26 W/(m K) for the neat resin was attributed to the difficulty of transferring thermal energy from fiber to fiber.

Better results were obtained by Lafdi and Matzek [26], who demonstrated an increase of thermal conductivity from 0.2 W/(m K) for epoxy resin to 2.8 W/(m K) for a 20 wt% VGCNF composite. These results indicate that, unlike strength or stiffness, good coupling to the matrix is not necessary to achieve high thermal conductivity, making compounding less critical. The thermal conductivity values obtained for composites made from the oriented large diameter VGCF represent an upper limit for VGCNF composites and are thoroughly discussed in the review of Lake and Ting [12], giving good perspective on the upper limits of thermal conductivity expected for VGCNF composites.

T. Gibson et al. [56] have created VGCNF and silver plated VGCNF-filled adhesives that provide sufficient electrical conductivity and thermal conductivity for many aerospace applications.

#### **4.33 Coefficient of thermal expansion**

Graphite has long been known to have low thermal expansion [57], and the coefficient of thermal expansion of VGCF-epoxy composites has been shown to be substantially lower than that of the matrix [58], so we may presume that CTE reduction will be another field where VGCNF may contribute desirable improvements.

### **5. Applications**

Introduction of a new material is typically limited by a number of technical barriers. In the case of VGCNF, these barriers include surface functionalization for bonding to selected matrices, dispersion and orientation of the VGCNF in the composite, and lack of preforms or weaves which would facilitate utilization of VGCNF in composite articles. Even though vigorous efforts of numerous researchers have overcome several of the most daunting of these barriers and have established a foundation of rules for composite synthesis needed for the emergence of commercial applications, much work remains before such composite technology is reduced to standard industrial practice.

To surmount the risks and capitalize on benefits attendant to use of VGCNF at this juncture, manufacturers must be able to visualize unique solutions to otherwise insoluble problems. When desired properties overlap those properties offered by submicron graphitic reinforcements, (as in solving the delamination problem), VGCNF looms as an immediate practical solution

When a designer considers replacing a metal part with a composite component, thermal and electrical performance may often be of critical importance. Inadequate heat dissipation, EMI shielding, and electrical grounding will often prevent exchange of a

lighter composite for a heavier metal part, even though weight-sensitive niche applications can often tolerate the higher nanocomposite cost. The aerospace industry in particular has many such applications - particularly in satellites. The competing technology, the addition of metal powders, may result in unacceptable corrosion and impact strength degradation.

Prototypes incorporating VGCNF have been fabricated from thermoplastics, thermosets, and elastomers. While it would be desirable to achieve fully multifunctional performance yielding improvements in mechanical properties as well as thermal and electrical characteristics, there are many applications where the thermal and electrical benefits alone justify the use of VGCNF.

The necessity of going beyond conventional compounding techniques has created opportunity for the emergence of a supply chain producing VGCNF compounded materials. Resins are now available which contain 20 percent by weight loadings of VGCNF that can be utilized in a variety of formulated epoxy systems including pre-pregs, molding compounds, adhesives, and coatings ([nanospense.com](http://nanospense.com)). Such formulations are intended for use in conductive adhesives with high strength characteristics, structural composite panels to replace metal for weight savings and corrosion resistance, and components for medical, aerospace, and electronics applications. Use of VGCNF has been reported for improved mechanical properties of linerless composite pressure vessels, where performance improvement is attributed to the development of high strain, microcrack-resistant resins and the inclusion of VGCNF at the ply interfaces. These materials eliminate microcracking as the first failure mode and improve the laminate failure strain to a level that nearly equals that of the Toray T700 reinforcing fiber ([ctd-materials.com](http://ctd-materials.com)).



Finally, the availability of a thermal grease composed of a silicon-free carrier material incorporating VGCNF as the thermal conductor has also been announced (electrovac.com). Here the nano-scale filler enables accurate thin film application and decreases thermal resistance.

## **6. Summary and Conclusions**

This review has summarized the wide variety of composite properties achieved with VGCNF composites:

Compounded with thermoplastics or thermosets, VGCNF can more than triple the resin's tensile modulus and strength. Compressive strength is generally improved by an even larger margin. Preliminary research gives some hope that a practical method may be found to improve the orientation of VGCNF to achieve even greater improvements. Perhaps the most beneficial application of VGCNF is to add conductivity to plastic matrices. Resistivities of below  $0.15 \Omega \text{ cm}$  may be achieved with a fiber loading near 15 wt%, and a percolation threshold of below 1 wt% is possible. Furthermore, a tenfold improvement in thermal conductivity has been demonstrated in epoxy composites.

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### Figure Captions

Figure 1: Apparatus for manufacturing VGCNF

Figure 2: TEM showing the structure of a VGCNF with the cylindrical hollow core at the center.

Figure 3: TEM of the VGCNF wall showing the canted graphene planes comprising the “stacked cup” structure.

Figure 4: A clump of VGCNF

Figure 5: TEM of a VGCNF graphitized at 2800 °C.

Figure 6: Schematic of the structure of VGCNF at various stages of graphitization. Each box represents a section of a cylindrical wall.

Figure 7. Resistivities of some polypropylene/VGCNF composites. Approximate resistivity values required for static discharge, electrostatic painting, and radio frequency interference shielding are indicated. Data from three different types of fibers are plotted and compared to a simple superposition model for graphitized or as-grown fibers (Ref 44).

Figure 1

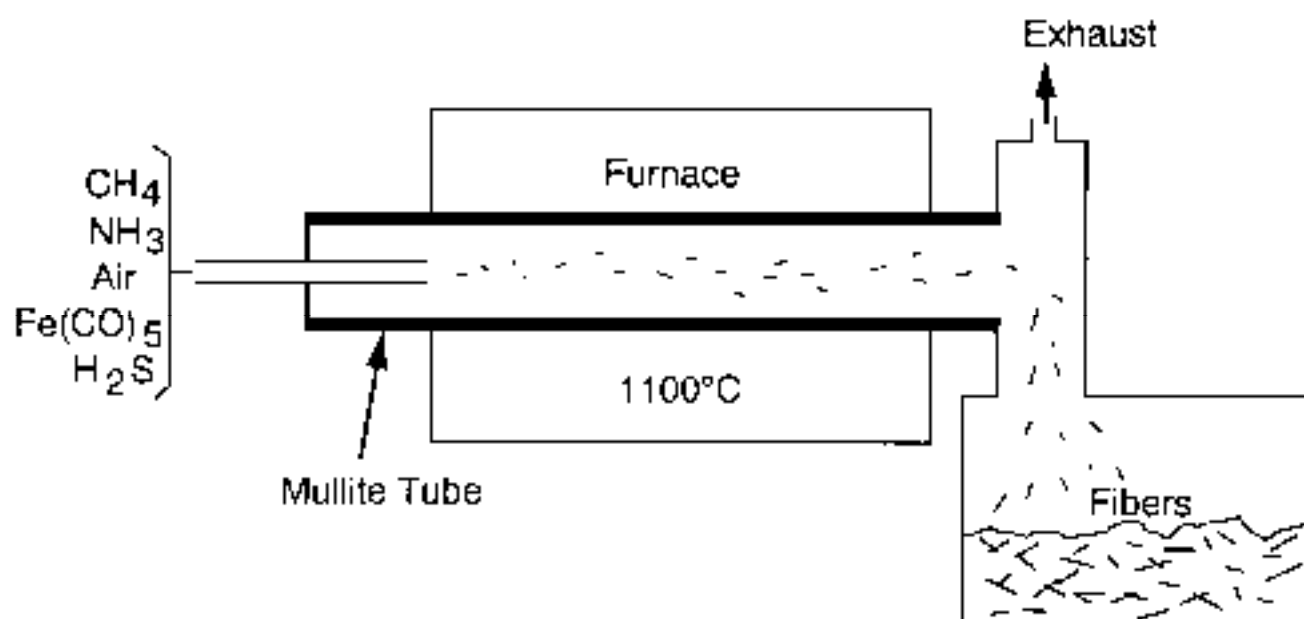


Figure 2

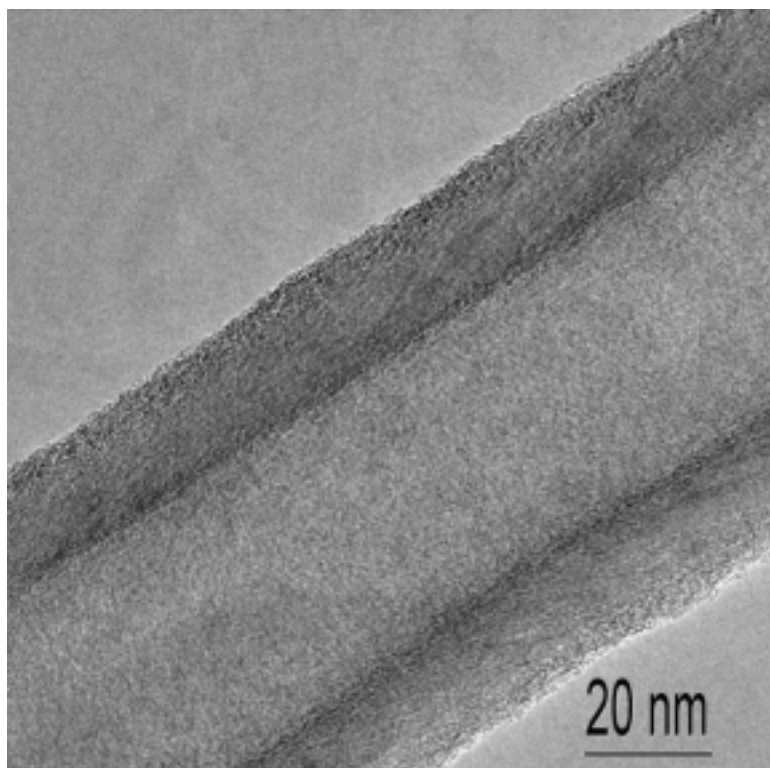


Figure 2

**Figure 3**  
[Click here to download high resolution image](#)

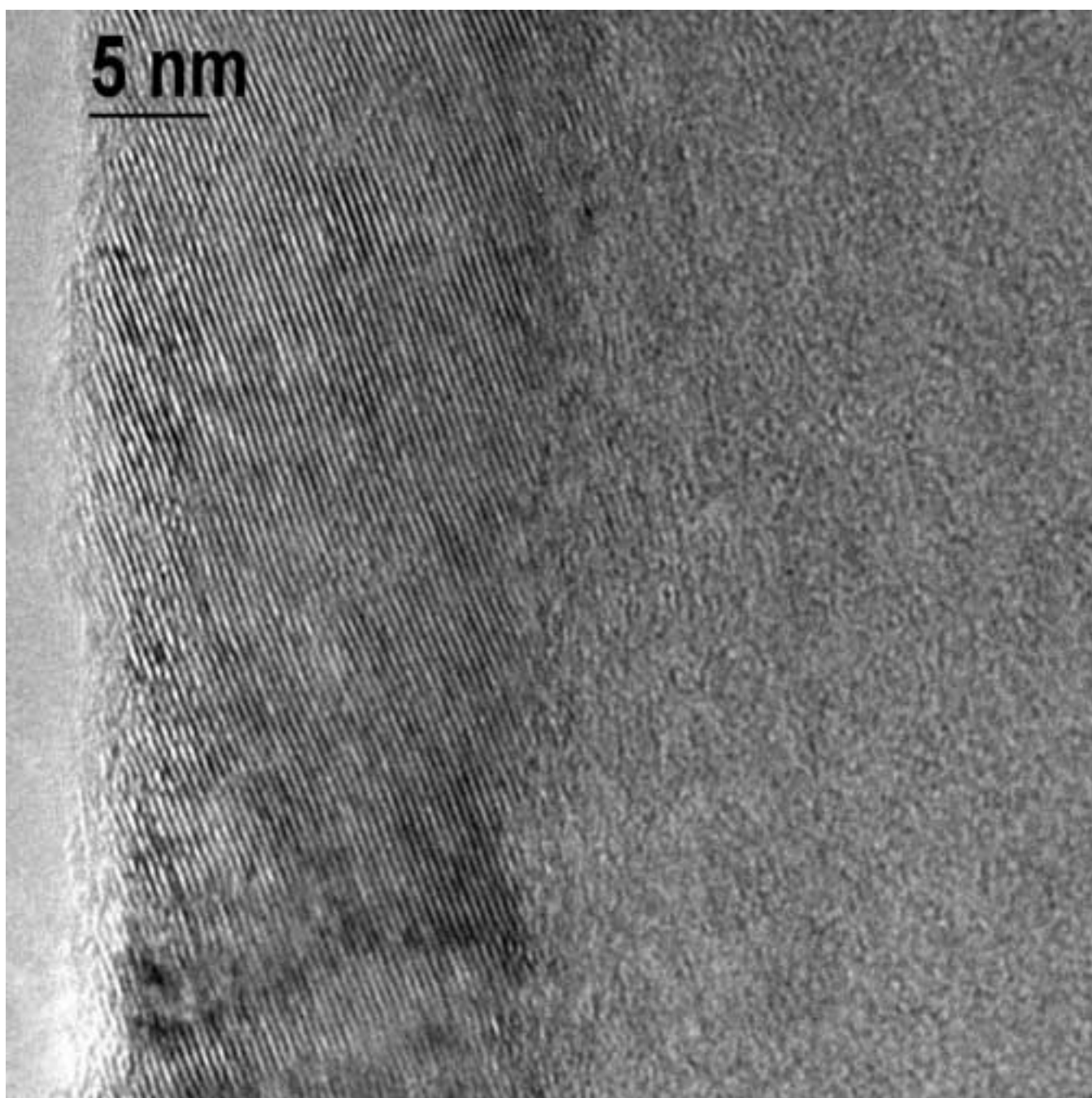


Figure 4

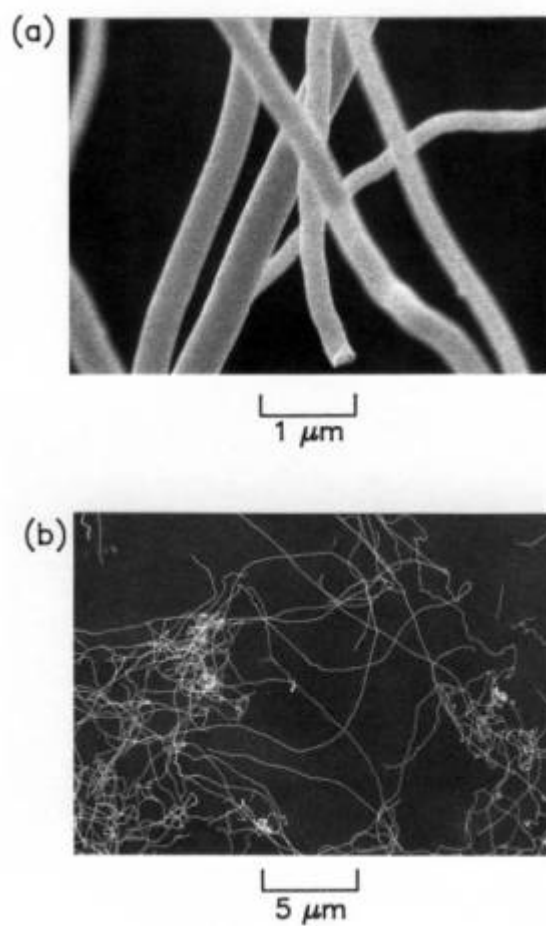




Figure 5 revised

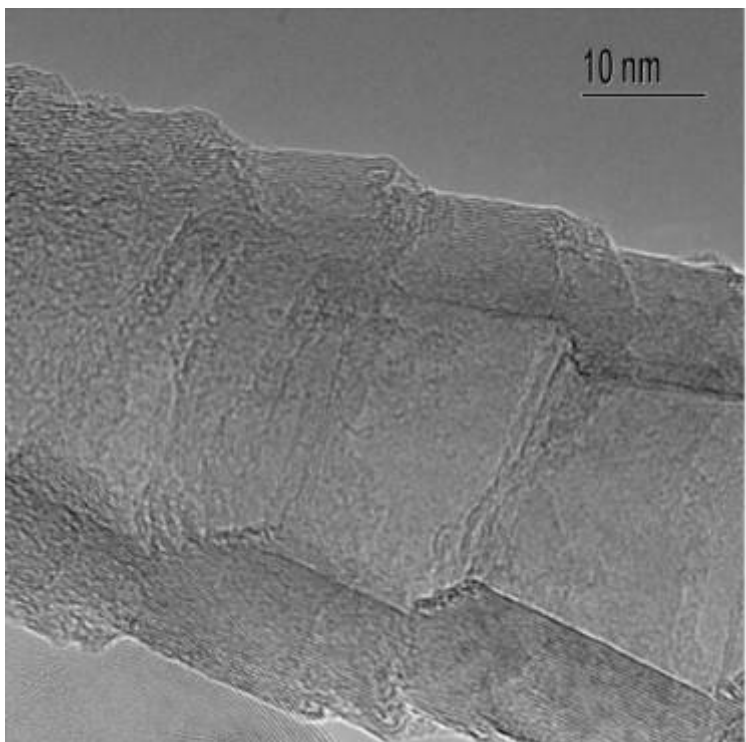


Figure 6

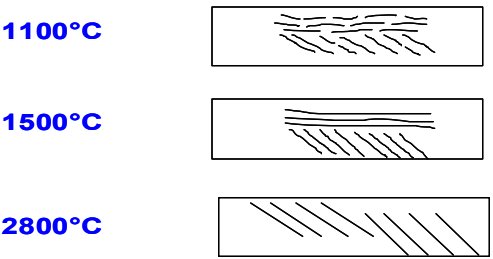


Figure 7

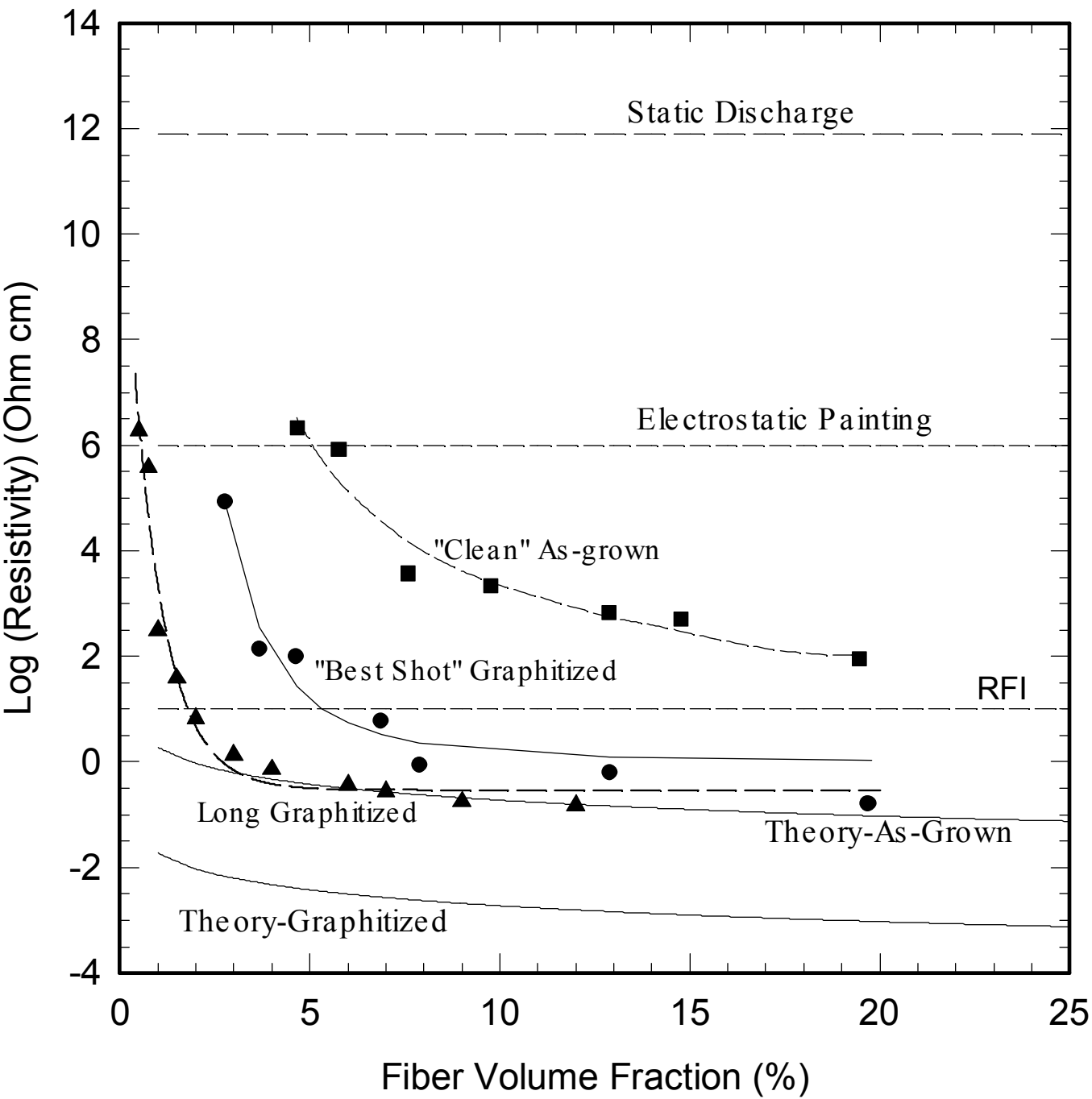


Figure 7

We would like to thank the two reviewers for their excellent and helpful suggestions: Reviewer 1 is to be commended for taking enough time to carefully read and evaluate the manuscript. We have taken all of his valuable suggestions.

Reviewer 2 is obviously an expert in the field and provided us with necessary new references and useful comments on how to amplify of the manuscript to cover new developments. We likewise took all of Reviewer 2's suggestions, adding 7 new references.